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NPDES Compliance Monitoring Inspector Training: Sampling Procedures

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NPDES Compliance Monitoring Inspector Training

Sampling Procedures

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16. ABSTRACT

This document is part of a set of five documents which make up the National Pollutant Discharge Elimination System (NPDES) Compliance Monitoring Training Program. The training modules were developed by the Environmental Protection Agency (EPA), Office of Water Enforcement and Permits (OWEP), to instruct NPDES inspectors in various aspects of conducting NPDES Compliance Monitoring Inspections. The five training modules in this set are: 1) Overview, 2) Legal Issues, 3) Biomonitoring, 4) Sampling Procedures, and 5) Laboratory Analysis.

The modules were designed to be used as a self-taught course or as the basis for a lecture course to supplement on-the-job training for NPDES Inspectors. The modules should be presented by experienced and knowledgeable staff who can answer any questions, discuss policies regarding the topic being presented, and conduct on-the-job training. Each module covers a specific aspect of a compliance inspection. Instructors for a particular module may be selected according to their expertise, and training sessions could be scheduled based on the needs, the resources, and the time available to the Region. The modules can be presented individually or as a complete package.

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NPDES COMPLIANCE MONITORING

INSPECTOR TRAINING MODULE

SAMPLING PROCEDURES

U.S. ENVIRONMENTAL PROTECTION AGENCY

ENFORCEMENT DIVISION

OFFICE OF WATER ENFORCEMENT AND PERMITS

COMPLIANCE BRANCH

JUNE 1980

U.S. ENVIRONMENTAL PROTECTION AGENCY

COMPLIANCE MONITORING INSPECTOR TRAINING

DISCLAIMER

This module has been reviewed by the Office of Water Enforcement and Permits, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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These modules were developed by Barbara A. Schick, Claire M. Gesalman, Duane Geuder, Edward Bender, and with contributions by Dave Shedroff, all of whom are staff members of the Enforcement Division, Office of Water Enforcement and Permits. The Compliance Branch, Enforcement Division, Office of Water Enforcement and Permits, wish to express their appreciation to the secretarial staff for the assistance provided in the preparation of this module, especially Mrs. Mary F. Rogers and Mrs. Wilma Haney.

LIST OF HANDOUTS

1. GLOSSARY
2. RECOMMENDATION FOR SAMPLING AND PRESERVATION OF SAMPLES ACCORDING TO MEASUREMENT
3. STANDARD ANALYTICAL TEST METHODS
4. CRITERIA FOR SELECTING AUTOMATIC SAMPLERS
5. PROCEDURES FOR CALIBRATING FIELD EQUIPMENT
6. CHAIN-OF-CUSTODY RECORD
7. SAMPLE LABEL FORMATS

FOREWORD

The National Pollutant Discharge Elimination System (NPDES) Compliance Monitoring Inspector Training Modules were developed by the Environmental Protection Agency (EPA), Office of Water Enforcement and Permits (OWEP), to instruct NPDES inspectors in various aspects of conducting NPDES Compliance Monitoring Inspections.

The EPA Regions have identified a need for training materials to instruct new employees in conducting NPDES inspections. Training seminars that are currently offered either do not address the training needs of an NPDES inspector or are not available due to limited resources or conflicting course schedules. These training modules were developed to fill the Regions' need for in-house inspector training.

The objectives of the training modules are:

1. To acquaint new inspectors with the NPDES Compliance Inspection program;

2. To serve as a refresher course for experienced NPDES Inspectors;

3. To assure consistency in the NPDES Compliance Inspection program; and

4. To inform and instruct inspectors concerning new inspection procedures.

The modules were designed to be used as a self-taught course or as the basis for a lecture course to supplement on-the-job training. The modules should be presented by experienced and knowledgeable Regional staff who can answer any questions, discuss Regional policies regarding the topic being presented, and conduct on-the-job training.

The module format was chosen for this training program because of its flexibility. Each module covers a specific aspect of a compliance inspection. Instructors for a particular module may be selected according to their expertise, and training sessions could be scheduled based on the needs, the resources, and the time available to the Region. The modules can be presented individually or as a complete package.

An outline of information contained in the individual training modules is listed below. There are currently five NPDES Compliance Monitoring Inspector Training modules:

1. The Overview module gives the inspector an overview of the compliance program and a brief summary of the different types of compliance inspections.

FOREWORD (Continued)

2. The Legal Issues module outlines the legal issues which must be addressed during an inspection and legal information that will assist inspectors in performing their duties.

3. The Biomonitoring module outlines the principles of biomonitoring and the role of biological testing in the inspection program.

4. The Sampling module details the sampling procedures that an inspector uses when conducting a sampling inspection.

5. The Laboratory Procedures module outlines the procedures and information necessary for an inspector to perform an effective evaluation of a permittee laboratory.

The layout of the text of each module is on a half page so that students may include their notes with the text.

These training modules were developed for the Regions and are designed to be used by the Regions for in-house training. If these modules are to be a success, the Regions must participate in their ongoing development. This can be accomplished by providing EPA Headquarters with changes or information which Regional instructors or managers believe would improve the modules. The format of the modules can be updated and revised at OWEP as the need arises as they were developed and produced at EPA Headquarters. Cooperation and commitment to training by the Regions will promote the development of a useful training document.

These training modules were developed primarily for Regional NPDES Inspectors; but they are also available to other interested parties such as State offices, attorneys, other program offices, facility owners and operators, and members of the general public.

Comments, information, and suggestions to improve the modules should be addressed to the:

Technical Evaluation and Support Section (EN-338)
Office of Water Enforcement and Permits
U.S. Environmental Protection Agency
401 M Street, SW
Washington, D.C. 20460

Modules covering new topics may be added to the existing ones as the need arises. Subject suggestions for future modules should be sent to the above address.

Requests for training modules will be handled at the above address depending on available supplies.

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U.S. ENVIRONMENTAL PROTECTION AGENCY

COMPLIANCE MONITORING INSPECTOR TRAINING MODULE: SAMPLING PROCEDURES

NOTES	LESSON
I. INTRODUCTION	I. INTRODUCTION
Background	A. Background
	The Federal Water Pollution Control Act Amendments of 1972 established the objectives of restoring and maintaining the chemical, physical, and biological quality of the Nation's water. To achieve those objectives, the Act set a goal of eliminating the discharge of pollutants into navigable waters by 1985; and Section 402 of the Act established the National Pollutant Discharge Elimination System (NPDES), under the Environmental Protection Agency (EPA), as the principal mechanism for reducing the discharge of pollutants.
	NPDES discharge permits have been issued to more than 50,000 municipal and industrial pollutant dischargers. These permits contain four primary elements:
Elements of a Permit	1. Interim effluent limitations governing effluent discharges during treatment facility construction activities; 2. Final effluent limitations reflecting the required treatment levels; 3. Schedules for the construction and completion of treatment facilities for achieving final effluent limitations; and 4. Reporting requirements relating to compliance with milestones contained in the construction schedules and with self-monitoring of the effluent limitations. Self-monitoring requirements

NOTES	LESSON
	specify which parameters are to be monitored, the sample type, and the monitoring and reporting frequency.
	Compliance with the NPDES permit is assessed by EPA and the States through a program of self-monitoring report reviews and facility inspections.
Handout 1: Glossary	A glossary of terms associated with sampling procedures and equipment is shown in Handout 1.
Objectives of Sampling	B. Objectives of Sampling
	A facility inspection encompasses many activities, from review of self-monitoring and analytical laboratory records to actual sampling. This module deals with sampling activities. Other activites will be, or have been, discussed in other modules.
	Your sampling activities as NPDES inspectors will be conducted to accomplish one or more of the following objectives:
	1. Verify compliance with effluent limitations
	2. Verify self-monitoring data
	3. Verify that parameters specified in the permit are consistent with wastewater characteristics
	4. Support permit reissuance and revision
	5. Support enforcement action.

NOTES	LESSON
Sampling Inspection Tasks	C. Sampling Inspection Tasks In order to achieve the sampling objectives, you must perform one or more of the following tasks: 1. Sample at the location and for the parameters specified in the NPDES permit 2. Sample at locations and for parameters not specified in the NPDES permit, as requested by enforcement personnel (this may require informal consent of the permittee) 3. Verify operation and calibration of monitoring equipment 4. Measure flow either by verifying accuracy of in-plant equipment or by actual independent flow measurement Your sampling inspection should also verify that the: 1. Permittee's sampling location(s) includes all the effluent from process and nonprocess wastewater system(s) 2. Sampling location specified in the permit is adequate for the collection of a representative sample of the wastewater 3. Permittee's sampling technique is adequate to ensure the collection of a representative sample 4. Permit sampling and monitoring requirements will yield representative samples

NOTES	LESSON
	5. Parameters specified in the permit are adequate to cover all pollutants of concern that may be discharged by the permittee
Compliance Sampling Protocols	D. Compliance Sampling Protocols You must exercise extreme care to ensure that all sampling efforts comply with quality assurance practices and chain-of-custody procedures discussed later in this module. IN ADDITION, ALL COMPLIANCE INSPECTION ACTIVITIES SHOULD BE CONDUCTED ON THE PREMISE THAT THEY MAY LEAD TO AN ENFORCEMENT ACTION.
II. SAMPLE COLLECTION	II. SAMPLE COLLECTION
Introduction	A. Introduction The actual sample collection is an extremely important part of any compliance sampling inspection. Without the use of proper sample collection techniques, the most precise and accurate analytical procedures are useless and the results of the inspection may be invalid. In addition, the flow and composition of the waste streams you will be sampling during a compliance inspection will vary. In a plant using continuous processes or in a municipal treatment facility, the period of variation will be long. In plants where production is seasonal or batch processes are used, the period of variation is much shorter, sometimes instantaneous. In order to accommodate the variety of conditions that exist and to ensure that representative samples are collected and properly handled, you should perform a

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	reconnaissance of the site, if necessary, and prepare a sampling study plan.
Monitoring Study Plan	B. Monitoring Study Plan To develop a monitoring study plan, you will need: 1. EPA guideline materials; 2. A copy of the NPDES permit; 3. A knowledge of the waste treatment processes employed; 4. A knowledge of the production processes employed or, in a municipal plant, a knowledge of the raw waste; (For industrial processes, the EPA development documents are a good source of information. A plant flow diagram is also useful.) 5. A knowledge of travel and shipping schedules (airline schedules) in the area of the plant to be sampled; and (The availability of dry ice or chilling packs should be ascertained.) 6. A thorough knowledge of the Department of Transportation (DOT) shipping regulations as they apply to the constituents contained in your samples including the preservatives.
Items to Address in Sampling Plan	Your sampling plan should address the following items: 1. Pollutant parameters to be measured. The pollutant parameters that are specified in the NPDES permit

NOTES	LESSON
	will provide the basis for parameter selection. The permit specifies the pollutant parameters that must be monitored by the permit holder, and these parameters are given as mass or concentration-based discharge limitations. You will select these same parameters for compliance sampling, but you may select additional parameters if new processes or products have been incorporated in the plant or new or added sources of wastewater are in evidence. If new processes or products have been incorporated in the plant, additional sampling will help provide the basis for the necessary permit modifications. 2. Sampling sites. You should select sampling sites that correspond to the outfalls that appear in the NPDES permit. Additional sample sites other than those specified in the NPDES permit may also need to be sampled. 3. Sample volume*. The volume of samples you will collect depends on the type of sample collected, that is, grab or composite, and the type and number of analyses that are needed as reflected in the parameters to be measured. 4. Type of sample containers*. Your selection and preparation *All of these considerations must be closely coordinated with the laboratory(s) scheduled to perform the required analyses. Contact the laboratory(s) in advance of any sampling, go over your sampling plan, and ensure that all laboratory requirements will be met.

NOTES	LESSON
	of sample containers will be based on the parameters that are to be measured. 5. Sample preservation techniques*. In addition to providing temperature control as needed to preserve samples, you must also determine and provide the appropriate chemicals for sample preservation. Preservation techniques and prescribed holding times are specified in 40 CFR 136. 6. Sample identification format*. You must provide an acceptable identification label for each container so that each sample can be tracked accurately, and an uninterrupted chain-of-custody can be maintained. 7. Sample delivery schedules*. Once it is collected, you must arrange for the sample to be delivered to the laboratory for analysis within the prescribed holding time period. This may be dependent on the local airline or ground transportation schedules. 8. Procedures for potentially hazardous samples*. Samples of effluent or process waste that are potentially hazardous, samples with extremely high or low pH, and samples that may contain extremely toxic, volatile, or explosive substances will require special handling. 9. Chain-of-custody procedures*. You must prepare chain-of-custody

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	report forms that will be necessary for evidentiary purposes.
Considerations in Sampling	C. Sampling Considerations Because varying conditions cannot be predicted for different sampling locations, you will have to compensate for these differences to collect representative samples. However, there are basic considerations that will guide you in the collection of samples. First, you should collect samples where the wastewater flow is well mixed. The most desirable sample collection point is the area of greatest turbulence; skimming of the water surface or dragging the channel bottom should be avoided unless you are specifically sampling for oil and grease or sediments. Stilled areas should be avoided, particularly if the wastewater contains immiscible liquids or suspended solids. Second, you should collect samples from the center of the stream. Unless samples are to be drawn from a wide conduit, collect them from the center of the flow. Ideally, the entire wastewater flow should be captured, for example, for 6-inch or 8-inch pipes, into a wide-mouthed sample container. Wide conduits or paths of flow may require dyeing to determine the most representative sampling site. If dyeing is not performed or is inconclusive, consider cross-sectional sampling. The most representative samples will be drawn from a depth of 40 to 60% of the total depth of the wastewater. Grab samples for analysis of oil and grease or other immiscible pollutants should not be transferred from the sampling container. These single-dip samples must be analyzed separately to avoid the loss of pollutants. Avoid

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Information on Oil and Grease	subdividing the sample in the laboratory. When information is required about the average grease concentration of a waste over an extended period, examine individual portions collected at prescribed time intervals to eliminate losses of grease on sampling equipment during collection of a composite sample. As mentioned earlier, samples should be collected at the location specified in the NPDES permit. However, in some instances this specified location may not be adequate for the collection of representative samples, and you may determine that a better and more representative sample location exists. This judgment must be based on your knowledge of the plant, the production processes, and the outfalls. If a conflict as to the most representative site exists, collect samples at both sites. The reason for the conflict should be thoroughly documented for later resolution by the permitting authority.
Sample Locations	You should sample the influent to the wastewater treatment facility when this is specified in the permit. The preferred sample collection locations are those that provide the best mixing. These include the: 1. Aerated grit chambers 2. Upflow siphon following a comminutor in the absence of a grit chamber 3. Upflow distribution box following pumping from the main plant wet well 4. Flume throat 5. Pump wet well

NOTES	LESSON
	You should collect these samples upstream of any sludge or supernatant recirculation. Dechlorination of wastewater should be done to avoid prolonged, unrepresentative disinfection. If you are collecting wastewater samples from a pond or lagoon, composite samples should be taken. Although ponds and lagoons may have extremely long detention times, which may reduce or eliminate concentration fluctuations, the tendency of these bodies to short circuit or to release batches of algae makes composite sampling advisable in the absence of information to the contrary. Bodies of water that have the inlet and outlet located near one another are likely to short circuit. Grab samples may be employed if past experience or dye studies indicate a homogeneous discharge.
Sample Volume	D. Sample Volume The volume of the collected and properly preserved sample should be sufficient to perform all the analyses required in the sample study. The minimum volume will have been established through your coordination with the laboratory scheduled to perform the analyses.
Volume Requirements **Handout 2: List of Minimum Volume Requirements and Preservation Methods**	Volume requirements for individual analyses range from 25 milliliters for pH and organic carbon determinations to 1,000 milliliters or more for BOD, oil and grease, settleable matter, and temperature determinations. Refer to Handout 2 for a list of minimum volume requirements, but the ultimate authority is the receiving laboratory.

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	Parameters which have identical collection and preservation requirements should be grouped into the same container(s) to minimize work and number of contrainers.
Selections and Preparation of Sample Containers	E. Selection and Preparation of Sample Containers It is essential that the sample containers be made of chemically resistant material that do not affect the concentrations of the pollutants to be measured. The sample containers that you will be using will usually be either glass or plastic (see CFR 136). For most analyses, the option or using either glass or plastic sample containers is open, and the selection of the sample container is based on whether the container material will affect pollutant concentrations of the sample. The lids and liners for the containers must be inert so that they do not interfere with the pollutant parameters to be measured. If either type of sample container is acceptable, plastic ones are preferred because they are less likely to break. Plastic sample bottles are usually made of polyethylene; but Teflon bottoms that provide added chemical resistance to strong mineral acids or organic solvents are available, although this added chemical resistance is not normally needed. Glass sample bottles are required when collecting samples for oil and grease, phenolics, or odor determinations. Plastic sample bottles are required when silica analysis is to be performed on the sample. Strong acids used as preservatives can react with polyethylene containers and should always be added to a comparatively large sample (see CFR 136.3 for required containers). As with the sample volume, be sure to use the sample container prescribed by the

NOTES	LESSON
	receiving laboratory so long as it does not conflict with CFR 136.3.
Sampling Techniques	F. Sampling Techniques The two types of sampling techniques that you will be using are grab and composite. Each technique is used to provide different data and to achieve different objectives.
Grab Samples	A grab sample is an individual sample collected over a period of time not exceeding 15 minutes. Grab samples are used to represent the conditions that exist at the moment of sampling and do not represent conditions at any other time. You will use grab samples to characterize the wastewater stream at a particular instant. Grab samples may be dictated by the NPDES permit. You should use these samples to determine consistency between the plant's self-monitoring data and the terms of the permit. In addition, other objectives may be satisfied with grab samples. For example, in cases where composite samples are mandated, you may also want to collect grab samples to corroborate the results of the composite samples. In lieu of direct field measurement, grab samples must often be used for evaluating parameters that are immediately affected by biological, chemical, or physical interactions. You may often use grab samples when analyzing for pH, temperature, residual chlorine, or dissolved oxygen, and these samples should be analyzed immediately. Oil and grease, and bacteriological samples are always taken by individual grab samples.

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Composite Samples	A composite sample is composed of a number of discrete samples taken during the compositing period. These samples may be collected individually at equal time intervals if the flow rate of the sample or stream does not vary widely, for example, plus or minus 15%, or they may be collected proportional to the flow rate. Flow or time proportioning may be dictated by the permit. You will use composite samples to characterize wastewater streams that are highly variable in pollutant concentration or flow rate. The analytical results of a composite sample yield the average pollutant parameter concentration in the wastewater stream during the compositing period. NPDES permits may be written such that the limitations are based on the average discharge concentration or on mass-based limitations. In both cases, a composite that meets the permits conditions and that fairly represents the wastewater should be taken.
Methods for Collecting Composite Samples	Various methods for collecting composite samples are available. One compositing method is continuous sampling at a constant rate. This method essentially collects a small side stream, and is not widely used because it yields excessively large sample volumes and may not be representative where variable flows are to be sampled. A second compositing method also involves continuous sampling, but it differs from the first method in that the sample pumping rate varies proportionally to the flow of the sampled stream. This type of sample can be collected by a variable speed positive displacement pump. This compositing method yields large representative sample volumes, but is not widely used due to the high cost of equipment.

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	The remaining methods involve periodic collection and combination of individual sample aliquots. One such compositing method yields a single sample composed of discrete sample aliquots that are collected in one container at constant time intervals. This method is widely used by both automatic and manual samplers. It provides representative samples when the flow of the sampled stream is constant or when the sample volume is manually adjusted for varying flow prior to being added to the composite sample container. Another compositing method provides for the collection of a constant sample volume at time intervals that are proportional to stream flow, (e.g., 200 ml of sample collected for every 5,000 gallons of stream flow). This compositing method provides representative samples of all waste streams when flow is measured accurately. You will use this method most frequently because it ensures representative samples and allows maximum utilization of the automatic sampler. Another method also allows for collection of discrete samples at constant time intervals. The volume of these samples is proportional to the total stream flow since the last sample. This method is not widely used because most automatic samplers do not provide for it.
Sample Preservation	G. Sample Preservation The majority of the pollutants in the samples collected are unstable to some extent. This instability requires that either the sample be analyzed immediately or that it be preserved or fixed to prevent (or minimize) changes in the pollutant concentrations between the time of collection and the time of analysis.

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	Because immediate analysis is not always possible, most samples are preserved regardless of the time of analysis. Additional problems may be encountered when 24-hour composite samples are collected. Sample deterioration can take place during the compositing process, and you will find it necessary to preserve or stabilize the samples during compositing in addition to preserving aggregate samples before shipment to the laboratory. Note that samples are to be preserved immediately upon sample collection unless precluded by the use of certain automatic samplers. Preservation techniques vary depending on the pollutant parameter that is to be measured. When the preservation techniques for one parameter may affect the analytical results of another parameter, you should collect discrete samples for each preservation technique. Familiarity with 40 CFR 136, particularly the proposed revisions, is essential to ensuring proper preservation techniques.
Sample Preservation Techniques	Sample preservation techniques include refrigeration, pH adjustment, disinfection, and chemical fixation. Refrigeration is the most widely used method and requires that the sample be quickly chilled to a temperature of 4°C, which retards bacterial action and suppresses the volatilization of dissolved gases and organic substances. The temperature should be verified and recorded during compositing. The temperature should not go below 4°C.
Handout 2: Preservation Methods and List of Minimum Volume Requirements	A detailed list of the preservation methods can be found in Handout 2.

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Analytical Methods	H. Analytical Methods The pollutant parameter values must be determined by one of the standard analytical methods shown in Handout 3 or by an alternate test procedure approved by the Regional Administrator. The actual analysis of the collected sample is not usually a task that you will perform. The exception to this is determining parameters that cannot be preserved. The most common parameters for which you will have to test are temperature, dissolved oxygen, and pH.
Handout 3: Standard Analytical Test Methods	
Instantaneous Measurements	Measurement of parameters that cannot be preserved should be taken at the beginning of the sampling cycle so that if violations or problems are identified, you have the option of taking additional measurements or collecting additional information during the remainder of the inspection.
Temperature	Temperature determinations may be made with any good grade mercury-filled or dial-type centigrade thermometer or thermistor. All temperature measuring devices mercury device must be calibrated periodically with a precision thermometer certified by the National Bureau of Standards. Temperature measurements should be taken in situ, if possible.
Dissolved Oxygen	You will usually use the probe, or electrode method for in-situ dissolved oxygen determinations. The sample size for this type of determination is 300 milliliters. No specific probe is recommended. However, some types that are used frequently and have been shown to be reliable are the Weston and Stack DO Analyzer Model 30, the Yellow Springs Instrument (YSI) Model 54,

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	and the Beckman Field Lab Oxygen Analyzer. These dissolved oxygen probes are temperature sensitive, and temperature compensation is usually built in. Make sure the probe does not dry out.
pH	pH determinations are always conducted during a sampling inspection. Arrangements must be made to have an appropriate pH meter available. A recording pH meter may be required by the NPDES permit and should be examined for accuracy.
Chlorine	In addition to temperature and dissolved oxygen field determinations, field chlorine determinations are sometimes needed. When chlorine determinations are deemed necessary in the planning stage, you must arrange to have the necessary analytical equipment at the sample site. A field kit is available for the amperometric technique of chlorine determinations.
Sample Identification	Each sample that is collected for laboratory or field analysis must be accurately and completely identified. An important feature of any label that you choose is that it be moisture resistant and properly fixed to the container. The information that the label should contain is discussed in detail in the quality assurance section of this module.
III. MANUAL SAMPLING	III. MANUAL SAMPLING
	Widemouthed bottles with openings at least 2 inches in diameter can be helpful for collecting manual samples to allow for rapid sample collection. These bottles should have a capacity of 1 to 4 liters to provide sufficient sample volume for analysis.

NOTES	LESSON
	Stainless steel buckets attached to a rope can be used for sampling in deep manholes or other difficult areas. Point samplers, weighted bottles that can collect samples at a specific depth, are also used for manual sampling. You must cork the weighted bottle and lower it into the waste stream to the desired depth, remove the cork using another line, and collect the sample. This is typically used for dissolved oxygen determinations. Hand-operated pumps provide an acceptable method for obtaining samples from inaccessible locations, but possible contamination by the pump and/or tubing must be carefully controlled.
IV. AUTOMATIC SAMPLERS	IV. AUTOMATIC SAMPLERS
Subsystem Components	A. Subsystem Components The automatic samplers with which you will be provided have five interrelated subsystem components. These components are: 1. Sample intake 2. Sample gathering 3. Sample transport 4. Sample storage 5. Controls and power.
Sample Intake Subsystem	The sample intake reliably gathers representative sample from the sampling stream. This intake is usually the end of a plastic suction tube. You may find it necessary to fit the end of the tubing with a manifold device for drawing a sample at various depths or locations across the flow channel simultaneously. The tubing should be at least 1/4 inch inside diameter,

NOTES	LESSON
	which is large enough to lessen chances of clogging but small enough to maintain velocity to avoid settling of solids. It should be free from plugging and clogging, and resistant to physical damage from large objects in the flow stream. Non-leaching tubing is most often used and may be replaced for each composite sample. The end of this tubing should be fixed so that its sampling location can be maintained throughout the sampling period. The automatic sampler should provide for line purging after each sample is drawn to prevent contamination of subsequent samples.
Sample Gathering Subsystem	Various commercial samplers provide one of three basic sample gathering methods: mechanical, forced flow, and suction lift.
Mechanical Subsystem	Mechanical gathering subsystems are usually built into place and include devices such as cups on cables, calibrated scoops, and paddle wheels with cups. Although these systems may obstruct the stream flow, they also take into account site specific considerations such as very high sampling lifts and wide or extremely deep channel flows. Because of the mechanical system employed, these units require periodic inspection and maintenance. You will probably not use this type of sample gathering subsystem in the field, but you should evaluate these installations as part of your inspection.
Forced-Flow	Forced-flow gathering subsystems are often built into place as permanent sampling facilities; thus, like the mechanical gathering subsystems, they may obstruct the stream flow. They also require periodic inspection and maintenance. However, forced flow subsystems have the advantage of being able to sample at great depths. In addition, because this gathering

NOTES	LESSON
	system uses air pressure to transport the sample, it may be ideal for sample collection in potentially explosive environments. The Air Lift Automatic Sampler System is one type of forced-flow gathering subsystem that you may encounter during your sampling inspection.
Suction Lift Subsystem	The suction lift gathering subsystems are the most widely used type of sample gathering subsystem because they have greatest versatility, and they only minimally affect flow patterns. Suction lifts are limited to 25 vertical feet or less because of internal friction losses and atmospheric pressure. With all suction devices, when the pressure on a liquid that contains dissolved gases is reduced, the dissolved gases tend to pass out of the solution. Because the gases leaving the surface have entrained suspended solids, the surface layer of the liquid becomes enhanced with suspended solids. The first flow of any suction lift sampler should be discarded to avoid this problem. To minimize the concentration effect, you should collect at least 100 milliliters per sampling unit.
Sample Transport Subsystem	The sample is transported from the sample intake to the collection bottle by a plastic tube. This tube is referred to as the sample transport subsystem. This tubing should be at least 1/4 inch inside diameter to maintain adequate flow and to prevent plugging. The tubing should not be too large so that a velocity of at least 2 feet per second can be maintained. Care should be exercised

NOTES	LESSON
	to avoid sharp bends, kinks, and twists in the transport line. Automatic samplers usually provide a line purge after each sample is collected to ready the line for the next sample transfer. You should provide new transport tubing for each new sample site to prevent sample contamination.
Sample Storage Subsystem	The sample storage subsystem can accommodate either a single large collection bottle or a number of smaller (400-milliliter) collection bottles. The total sample volume storage capability should be at least 2 gallons (7.6 liters), and some samplers have a capacity as great as 5 gallons. For preserving the samples, storage subsystems should also be large enough to provide space for ice to chill the sample after collection. Samples with individual bottles for discrete collection are usually equipped with a cassette which rotates to fill the bottle at the time of sampling. As mentioned before, whether large composite or discrete samples are collected, it is necessary to use collection bottles made of the appropriate materials.
Controls and Power Subsystem	The automatic samplers that are most widely used have solid state controls that are encapsulated. This minimizes the effects of the highly unfavorable environments that may be encountered in the field such as high humidity and corrosiveness. These units are also sealed so that they may be used with minimum risks in potentially explosive environments. Sealed units also protect the controls if the sampler is accidentially submerged. The control units allow you to select the time or flow compositing method, or continuous sampling method.

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	The power supply for most units is either alternating or direct (batteries) current. Alternating current is the most desirable power source because of its greater reliability. However, batteries can provide adequate power in remote areas. Automatic wastewater samplers may be subjected to rough use during the course of sampling, e.g., being dropped and submerged. To ensure reliable sampler operation, you should inspect and maintain the units at regular intervals.
Handout 4: Criteria for Selecting Automatic Samplers	If you are in a position to select an automatic sampler, the criteria listed in Handout 4 will serve as a useful guide.
Installation and Operation of Automatic Sampling Equipment	B. Installation and Operation of Automatic Sampling Equipment
Sampling Sites	Sampling equipment should be installed at sampling sites in which the flow is well mixed. You must select these sites with care in order to reduce the chance of injuries to sampling personnel. Use the buddy system when entering manholes or wet wells; do not enter these areas alone. Manholes or wet wells may flood or contain toxic or oxygen-depleted atmospheres. In addition, personnel entering poorly ventilated areas must be provided with proper clothing and protective equipment, such as acid-resistant boots, gloves, coats, and self-contained breathing apparatus.
Equipment Security	In exposed or unprotected areas where constant surveillance is not possible, you should lock or seal the samples to deter tampering with the samplers and sampling equipment or to detect tampering if it occurs.

NOTES	LESSON
Power Source	As mentioned before, most automatic samplers are capable of operating on both AC and DC. AC operation should always be chosen when it is available unless there are known irregularities in the power supply. AC operation is also more suitable for winter operation. Battery units are not reliable enough at extremely low temeratures. Battery operation should be reserved for remote sampling locations.
Sample Preservation During Compositing	When installing automatic sampling equipment, the following should be considered: 1. All samples should be kept at 4°C during the compositing period. (Freezing will destroy microbiological samples and alter nutrient concentrations.) 2. Most portable automatic samples contain ice compartments for sample chilling. 3. Separate sample chilling chambers can be provided for those samplers without the ice compartment.
Winter Operation	Cold weather can frustrate your best sampling efforts due to frozen transport lines, dead batteries, and sampler malfunctions. Recently, electrically heated transport lines have been used, but availability is poor and they are expensive. Smaller, more frequently collected samples will aid in keeping the transport lines open. Alternating current should be used to eliminate the effects of weak batteries. Heat may be provided for the sampling container by placing the sampler in a thermostatically controlled,

NOTES	LESSON
	electrically heated enclosure. In the absence of special equipment, freezing may be prevented by installing the sampler in a manhole or wet well or by wrapping the sampler with 8-9 inches of insulation and wind protection. Also, position the sampler well above the effluent stream so the tubing runs in a taut, straight line to prevent pooling of liquid.
V. QUALITY ASSURANCE	V. QUALITY ASSURANCE A quality assurance program must be included in all phases of the NPDES compliance sampling program. First, the role of quality assurance in the program from the time of sample collection through the presentation of evidence in court cases will be discussed and then quality assurance procedures in sample collection will be covered.
Purpose	A. Purpose The purpose of the NPDES compliance sampling program is to provide qualitative and quantitative data to determine whether individual permittees are in compliance with the requirements set forth in their permits. Inaccurate or incomplete sampling results can not be used as evidence in court. If the Region has established a quality assurance program, these procedures should be followed closely.
Objectives	B. Objectives 1. Obtain sampling results that are reproducible and consistent 2. Produce data that are complete, precise, accurate, and representative

NOTES	LESSON
Elements of a Quality Assurance Program	C. Elements of a Quality Assurance Program To achieve these objectives, the following elements will be included in the quality assurance program: ° Training. All members of the compliance sampling team should be trained in quality assurance procedures. ° Sample collection quality assurance. You should perform various control checks during actual sample collection. ° Chain-of-custody procedures. You and all members of your compliance sampling team should document completely the transfer of a sample from one person's custody to the next. ° Sample analysis quality assurance. Laboratory analysis equipment should be calibrated and control checks performed.
Quality Assurance in Sample Collection	D. Quality Assurance in Sample Collection Most errors in a sampling program can be traced to poor sample collection, preservation, and compositing techniques. For this reason, procedures have been developed that can be used as control checks. Duplicate samples provide a proficiency check for precision. You should bottle and seal duplicate samples using field sampling equipment installed at the sample site.

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	When automatic sampling equipment is not used, you should collect duplicate grab samples.
Split Samples	Split samples provide a method for comparing the laboratory procedures of the permittee with EPA laboratory procedures. Existing samples are divided into two segments for analysis in the separate laboratories. You can then evaluate statistically significant discrepancies in results and identify the cause.
Spiked Samples	Spiked samples provide a proficiency check for accuracy of the field sampling procedures. Known amounts of a particular constituent should be added to an actual sample or blanks of deionized water at concentrations where the accuracy of the test method is satisfactory. The amount added should be coordinated with the laboratory.
Sample Preservation Blanks	Sample preservation blanks provide a method for determining whether sample preservatives contain contamination. You should add a specified quantity of preservative (equal to that ordinarily added to a wastewater sample) to a sample of deionized water. After laboratory analysis, the value for the blank is subtracted from the sample value to obtain the actual value. (In the case of automatic sampling, run the deionized water through the sampler and then add the appropriate preservative.)
Calibration Plan	A calibration plan and documentation record should be prepared for all field analysis equipment. Refer to Handout 5 for a summation of the procedures to use for calibrating field equipment. You should keep a complete documentation record in your quality assurance logbook, including equipment specifications, calibration date, calibration expiration date, and
Handout 5: Procedures for Calibrating Field Equipment	

NOTES	LESSON
	maintenance due date. Automatic samplers should be calibrated for sample quantity, line purge, and timing.
Quality Assurance Precision Control Checks	Quality precision and accuracy control charts are graphic charts in which the vertical scale is plotted in units of the test result, and the horizontal scale is plotted in units of time or sequence of results. The upper and lower limits on the control chart are used for judging the significance of variation between duplicate samples. The central line represents the average value of the statistical measure being plotted. You must use mathematical equations to construct the control charts, and appropriate techniques for doing so can be found in EPA's Handbook for Analytical Quality Control in Water and Wastewater.
Reference: Handbook for Analytical Quality Control in Water and Wastewater	
Analyzing the Special Parameters	E. Analyzing the Special Parameters Certain parameters require special precautions in sample collection, preservation, and handling to maintain the integrity of the sample. These parameters include organics, acidity/alkalinity, dissolved parameters, mercury (total), phenolics, cyanides, sulfides, and sulfites. Handout 2 summarizes the special procedures required to maintain sample integrity for these parameters.
VI. CHAIN-OF-CUSTODY PROCEDURES	VI. CHAIN-OF-CUSTODY PROCEDURES In order to be able to use NPDES compliance sampling data in litigation, there must be accurate written records that trace the possession of a sample through all phases of the program. Custody refers to the possession of a sample. Chain-of-custody refers to the

NOTES	LESSON
	documented account of changes in possession that occur for a particular sample or set of samples.
Evidence	A. Evidence Recording chain-of-custody procedures facilitates their admission as evidence under Rule 803(b) of the Federal Rules of Evidence (P.L. 93-575). Written records of regularly conducted business activities may be introduced into evidence without the testimony of the persons who made the record. It is important that you follow the chain-of-custody procedures that will be discussed. Chain-of-custody should allow for an accurate and step-by-step recreation of the sample path, from origin through analysis.
Transfer of Custody and Shipment	B. Transfer of Custody and Shipment You will be responsible for properly packaging and dispatching samples to the appropriate laboratories for analysis. This includes filling out, dating, and signing the Chain-of-Custody Record. A recommended format for this record is shown in Handout 6.
Handout 6: Chain-of-Custody Record	
	When transferring the possession of samples, you must sign and record the date and time on the Chain-of-Custody Record (a signature, not initials is required). Although custody transfers ordinarily involve a group of samples, the record should account for each individual sample. To prevent undue proliferation of custody records, you should try to keep transfers to a minumum. You should include the Chain-of-Custody Records with the instructions for analyses when you ship samples to the laboratory. You should register them and request a return receipt. You should retain all receipts as part of the chain-of-custody documentation.

NOTES	LESSON
Sample Collection, Handling and Preparation	C. Sample Collection, Handling, and Preparation It is important to keep a precise record of sample collection and handling data. You should sign all field records containing these data at the time of collection. You should also document the following information in the field records: 1. Unique sample or log number 2. Date and time 3. Source of sample, including facility name, location and sample type 4. Preservative used 5. Analyses required 6. Name of collector(s) 7. Pertinent field data (pH, dissolved oxygen, chlorine residual, etc.) 8. Serial number on seals and transportation cases
Sample Label Information	Gummed labels or standardized tags should be attached to each sample. Each label should include the following information: 1. Sample identification number 2. Date and time of sample collection 3. Source of sample 4. Preservative used 5. Collector's initials
Handout 7: Sample Label Formats	Refer to Handout 7 for examples of sample label formats.

NOTES	LESSON
Sample Transportation	After the samples are properly labeled, they should be placed in the transportation case, (which complies with DOT regulations and related EPA guidance) along with the Chain-of-Custody Record Form, pertinent field record and the Analysis Request Form. You should then seal and label the transportation case. If you find that the use of a transportation case is inconvenient, you may place a tamper-proof seal around the cap of each sample. The samples should be packed in a synthetic ice substitute that will maintain sample temperature at 4°C. throughout shipment. For composite samples, you may transfer unsealed containers from one crew to the next. The receiving crew will sign for the samples thus verifying the list of samples that you have compiled.
Photographs	If you take photographs or color slides of the sample outfall location, you should keep a photograph log which includes the following information: 1. Your signature 2. Time and date 3. Site location 4. Brief description of subject.
VII. SUMMARY	VII. SUMMARY We have now covered various sampling procedures required for conducting a NPDES compliance sampling inspection. Review the handouts provided and consult you manuals before initiating an inspection.

GLOSSARY

Chain of Custody—The written record of the possession and handling of the wastewater sample, from collection through laboratory analysis and disposition of the analytical results and the unused sample remnants.

Comminutor—A sewage grinder, usually located at the beginning of the treatment process.

Composite Sample—A sample that is composed of at least eight discrete samples. The aggregate sample will reflect the average water quality over the compositing or sampling period.

Grab Sample—A sample that is collected over a time period not exceeding 15 minutes.

Instantaneous Measurements—In situ or grab measurements for such parameters as dissolved oxygen, pH, temperature, specific conductance, etc.

Quality Assurance—Refers to the procedures and practices used during sampling and analysis that ensure or provide proof of accuracy, reproducibility, and representativeness.

Spiked Samples—Effluent or blank samples to which a known quantity of another substance has been added.

Split Samples—Duplicate samples or samples that have been divided into two containers for analysis by separate laboratories.

Supernatant—The upper level of water or the overflow from a clarifier in a waste treatment plant.

RECOMMENDATION FOR SAMPLING AND PRESERVATION OF SAMPLES ACCORDING TO MEASUREMENT

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time
100 Physical Properties				
Color	50	P,G	Cool, 4°C	24 Hrs.
Conductance	100	P,G	Cool, 4°C	24 Hrs.
Hardness	100	P,G	Cool, 4°C HNO_3 to pH < 2	6 Mos.
Odor	200	G only	Cool, 4°C	24 Hrs.
pH	25	P,G	Det. on site	6 Hrs.
Residue				
Filterable	100	P,G	Cool, 4°C	7 Days
Non-Filterable	100	P,G	Cool, 4°C	7 Days
Total	100	P,G	Cool, 4°C	7 Days
Volatile	100	P,G	Cool, 4°C	7 Days
Settleable Matter	1000	P,G	None Req.	24 Hrs.
Temperature	1000	P,G	Det. on site	No Holding
Turbidity	100	P,G	Cool, 4°C	7 Days
200 Metals				
Dissolved	200	P,G	Filter on site HNO_3 to pH < 2	6 Mos.
Suspended	200		Filter on site	6 Mos.
Total	100	P,G	HNO_3 to pH < 2	6 Mos.

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time
Dissolved Oxygen Probe	300	G only	Det. on site	No Holding
Winkler	300	G only	Fix on site	4–8 Hours
Phosphorus Ortho-phosphate, Dissolved	50	P,G	Filter on site Cool, 4°C	24 Hrs.
Hydrolyzable	50	P,G	Cool, 4°C H_2SO_4 to pH < 2	24 Hrs.
Total	50	P,G	Cool, 4°C H_2SO_4 to pH < 2	24 Hrs.
Total, Dissolved	50	P,G	Filter on site Cool, 4°C H_2SO_4 to pH < 2	24 Hrs.
Silica	50	P only	Cool, 4°C	7 Days
Sulfate	50	P,G	Cool, 4°C	7 Days
Sulfide	500	P,G	2 ml zinc acetate	24 Hrs.
Sulfite	50	P,G	Det. on site	No Holding
400 Organics				
BOD	1000	P,G	Cool, 4°C	24 Hrs.
COD	50	P,G	H_2SO_4 to pH < 2	7 Days
Oil & Grease	1000	G only	Cool, 4°C H_2SO_4 or HCl to pH < 2	24 Hrs.
Organic carbon	25	P,G	Cool, 4°C H_2SO_4 or HCl to pH < 2	24 Hrs.
Phenolics	500	G only	Cool, 4°C H_3PO_4 to pH < 4 1.0 g $CuSO_4$/l	24 Hrs.
MBAS	250	P,G	Cool, 4°C	24 Hrs.

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time
Mercury Dissolved	100	P,G	Filter on site HNO_3 to pH < 2	38 Days (Glass) 13 Days (Hard Plastic)
Total	100	P,G	HNO_3 to pH < 2	38 Days (Glass) 13 Days (Hard Plastic)
300 Inorganics, Non-Metallics				
Acidity	100	P,G	None Req	24 Hrs.
Alkalinity	100	P,G	Cool, 4°C	24 Hrs.
Bromide	100	P,G	Cool, 4°C	24 Hrs.
Chloride	50	P,G	None Req.	7 Days
Chlorine	200	P,G	Det. on site	No Holding
Cyanides	500	P,G	Cool, 4°C NaOH to pH 12	24 Hrs.
Fluoride	300	P,G	None Req.	7 Days
Iodide	100	P,G	Cool, 4°C	24 Hrs.
Nitrogen				
Ammonia	400	P,G	Cool,4°C H_2SO_4 to pH < 2	24 Hrs.
Kjeldahl, Total	500	P,G	Cool, 4°C H_2SO_4 to pH < 2	24 Hrs.
Nitrate plus Nitrite	100	P,G	Cool, 4°C H_2SO_4 to pH < 2	24 Hrs.
Nitrate	100	P,G	Cool, 4°C	24 Hrs.
Nitrite	50	P,G	Cool, 4°C.	48 Hrs.

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time
NTA	50	P,G	Cool, 4°C	24 Hrs.

1. More specific instructions for preservation and sampling are found with each procedure as detailed in this manual. A general discussion on sampling water and industrial wastewater may be found in ASTM, Part 31, p. 72–82 (1976) Method D-3370.

2. Plastic (P) or Glass (G). For metals, polyethylene with a polypropylene cap (no liner) is preferred.

3. It should be pointed out that holding times listed above are recommended for properly preserved samples based on currently available data. It is recognized that for some sample types, extension of these times may be possible while for other types, these times may be too long. Where shipping regulations prevent the use of the proper preservation technique or the holding time is exceeded, such as the case of a 24-hour composite, the final reported data for these samples should indicate the specific variance.

4. If the sample is stabilized by cooling, it should be warmed to 25°C for reading, or temperature correction made and results reported at 25°C.

5. Where HNO_3 cannot be used because of shipping restrictions, the sample may be initially preserved by icing and immediately shipped to the laboratory. Upon receipt in the laboratory, the sample must be acidified to a pH < 2 with HNO_3 (normally 3 ml 1:1 HNO_3/liter is sufficient). At the time of analysis, the sample container should be thoroughly rinsed with 1:1 HNO_3 and the washings added to the sample (volume correction may be required).

6. Data obtained from National Enforcement Investigations Center-Denver, Colorado, support a four-week holding time for this parameter in Sewerage Systems. (SIC 4952).

(EPA. Methods for Chemical Analysis of Water and Wastes, March 1979.)

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ANALYSIS PROTOCOL

(A) 40 CFR Part 136

PART 136—GUIDELINES ESTABLISHING TEST PROCEDURES FOR THE ANALYSIS OF POLLUTANTS

Sec.

136.1 Applicability.
136.2 Definitions.
136.3 Identification of test procedures.
136.4 Application for alternate test procedures.
136.5 Approval of alternate test procedures.

AUTHORITY: Sec. 304(g) of Federal Water Pollution Control Act Amendments of 1972 86 Stat. 816, et seq., Pub. L. 92-500).

§ 136.1 Applicability.

The procedures prescribed herein shall, except as noted in § 136.5, be used to perform the measurements indicated whenever the waste constituent specified is required to be measured for:

(a) An application submitted to the Administrator, or to a State having an approved NPDES program, for a permit under section 402 of the Federal Water Pollution Control Act as amended (FWPCA), and,

(b) Reports required to be submitted by dischargers under the NPDES established by Parts 124 and 125 of this chapter, and,

(c) Certifications issued by States pursuant to section 401 of the FWPCA, as amended.

[38 FR 28758, Oct. 16, 1973]

§ 136.2 Definitions.

As used in this part, the term:

(a) "Act" means the Federal Water Pollution Control Act, as amended, 33 U.S.C. 1314, et seq.

(b) "Administrator" means the Administrator of the U.S. Environmental Protection Agency.

(c) "Regional Administrator" means one of the EPA Regional Administrators.

(d) "Director" means the Director of the State Agency authorized to carry out an approved National Pollutant Discharge Elimination System Program under section 402 of the Act.

(e) "National Pollutant Discharge Elimination System (NPDES)" means the national system for the issuance of permits under section 402 of the Act and includes any State or interstate program which has been approved by the Admin-

HANDOUT 3
(Continued)

TABLE I—*List of approved test procedures*[1]—Continued

Parameter and units	Method	1974 EPA methods	14th ed. standard methods	References (page nos.) Pt. 31 1973 ASTM	References (page nos.) USGS methods[2]	Other approved methods
METALS—Continued						
29. Arsenic—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total arsenic.					
30. Barium—Total, milligrams per liter.	Digestion [4] followed by atomic absorption.[5]	97	152		83	
31. Barium—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total barium.					
32. Beryllium—Total, milligrams per liter.	Digestion [4] followed by atomic absorption [5] or by colorimetric (Aluminon).	93	152 177		53	
33. Beryllium—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total beryllium.					
34. Boron—Total, milligrams per liter.	Colorimetric (Curcumin)	13	287			
35. Boron—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total boron.					
36. Cadmium—Total, milligrams per liter.	Digestion [4] followed by atomic absorption [5] or by colorimetric (Dithizone).	101	148 152	343	62	[6] (617),[5] (37)
37. Cadmium—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total cadmium.					
38. Calcium—Total, milligrams per liter.	Digestion [4] followed by atomic absorption; or EDTA titration.	103	148 159	343	66	
39. Calcium—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total calcium.					
40. Chromium VI, milligrams per liter.	Extraction and atomic absorption; colorimetric (Diphenylcarbazide).	99, 105	192		76 75	
41. Chromium VI—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for chromium VI.					
42. Chromium—Total, milligrams per liter.	Digestion [4] followed by atomic absorption [5] or by colorimetric (Diphenylcarbazide).	103	148 192	343 350	78 77	[6] (619)
43. Chromium—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total chromium.					
44. Cobalt—Total, milligrams per liter.	Digestion [4] followed by atomic absorption.[5]	107	143	343	80	[5] (37)
45. Cobalt—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total cobalt.					
46. Copper—Total, milligrams per liter.	Digestion [4] followed by atomic absorption [5] or by colorimetric (Neocuproine).	105	143 194	345 353	53	(615),[5] (37)
47. Copper—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total copper.					
48. Gold—Total, milligrams per liter.	Digestion [4] followed by atomic absorption.[5]					
49. Iridium—Total, milligrams per liter.	Digestion [4] followed by atomic absorption.[5]					
50. Iron—Total, milligrams per liter.	Digestion [4] followed by atomic absorption [5] or by colorimetric (Phenanthroline).	110	148 208	345 358	102	[6] (619)
51. Iron—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total iron.					
52. Lead—Total, milligrams per liter.	Digestion [4] followed by atomic absorption [5] or by colorimetric (Dithizone).	112	148 215	345	155	[6] (619)

See footnotes at end of table.

TABLE I.—*List of approved test procedures*[1]—Continued

Parameter and units	Method	1974 EPA methods	14th ed. standard methods	References (page nos.) Pt. 31 1975 ASTM	References (page nos.) USGS methods[2]	Other approved methods
METALS—Continued						
55. Lead—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total lead.					
54. Magnesium—Total, milligrams per liter.	Digestion [3] followed by atomic absorption; or gravimetric.	114	118 221	315	109	[4] (619)
53. Magnesium—Dissolved milligrams per liter.	0.45-micron filtration [3] followed by referenced method for total magnesium.					
56. Manganese—Total milligrams per liter.	Digestion [3] followed by atomic absorption [3] or by colorimetric (Persulfate or periodate).	116	118 225, 227	343	111	[4] (615)
57. Manganese—Dissolved milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total manganese.					
58. Mercury—Total, milligrams per liter.	Flameless atomic absorption.	113	122	338	[5] (31)	
59. Mercury—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total mercury.					
60. Molybdenum—Total, milligrams per liter.	Digestion [3] followed by atomic absorption,[6]	130		330		
61. Molybdenum—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total molybdenum.					
62. Nickel—Total, milligrams per liter.	Digestion [3] followed by atomic absorption [3] or by colorimetric (Heptoxime).	141	118	345	113	
63. Nickel—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total nickel.					
64. Osmium—Total, milligrams per liter.	Digestion [3] followed by atomic absorption.[6]					
65. Palladium—Total, milligrams per liter.	Digestion [3] followed by atomic absorption.[6]					
66. Platinum—Total, milligrams per liter.	Digestion [3] followed by atomic absorption.[6]					
67. Potassium—Total, milligrams per liter.	Digestion [3] followed by atomic absorption, colorimetric (Cobaltinitrite), or by flame photometric.	143	215 221	403	134	[4] (620)
68. Potassium—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total potassium.					
69. Rhodium—Total, milligrams per liter.	Digestion [3] followed by atomic absorption.[6]					
70. Ruthenium—Total, milligrams per liter.	Digestion [3] followed by atomic absorption.[6]					
71. Selenium—Total, milligrams per liter.	Digestion [3] followed by atomic absorption.[3] [6]	143	139			
72. Selenium—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total selenium.					
73. Silica—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by colorimetric (Molybdosilicate).	274	487	328	139	
74. Silver—Total,[7] milligrams per liter.	Digestion [3] followed by atomic absorption [3] or by colorimetric (Dithizone).	148	148 213		142	[4] (618) [8] (37)
75. Silver—Dissolved,[7] milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total silver.					
76. Sodium—Total, milligrams per liter.	Digestion [3] followed by atomic absorption or by flame photometric.	147	220	403	143	[4] (621)
77. Sodium—Dissolved, milligrams per liter.	0.45 micron filtration [3] followed by referenced method for total sodium.					

See footnotes at end of table.

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istrator, in whole or in part, pursuant to section 402 of the Act.

(f) "Standard Methods" means *Standard Methods for the Examination of Water and Waste Water*, 14th Edition, 1976. This publication is available from the American Public Health Association, 1015 18th Street, N.W., Washington, D.C. 20036.

(g) "ASTM" means *Annual Book of Standards, Part 31, Water, 1975*. This publication is available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

(h) "EPA Methods" means *Methods for Chemical Analysis of Water and Waste, 1974*. Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, Cincinnati, Ohio 45268; U.S. Environmental Protection Agency, Office of Technology Transfer, Industrial Environmental Research Laboratory, Cincinnati, Ohio 45268. This publication is available from the Office of Technology Transfer.

[38 FR 28758, Oct. 16, 1973, as amended at 41 FR 52781, Dec. 1, 1976]

§ 136.3 Identification of test procedures.

(a) Every parameter or pollutant for which an effluent limitation is now specified pursuant to sections 401 and 402 of the Act is named together with test descriptions and references in Table I. The discharge parameter values for which reports are required must be determined by one of the standard analytical methods cited and described in Table I, or under certain circumstances by other methods that may be more advantageous to use when such other methods have been previously approved by the Regional Administrator of the Region in which the discharge will occur, and providing that the Director of the State in which such discharge will occur does not object to the use of such alternate test procedures.

(b) Under certain circumstances the Regional Administrator or the Director in the Region or State where the discharge will occur may determine for a particular discharge that additional parameters or pollutants must be reported. Under such circumstances, additional test procedures for analysis of pollutants may be specified by the Regional Administrator, or the Director upon the recommendation of the Director of the Environmental Monitoring and Support Laboratory, Cincinnati.

(c) Under certain circumstances, the Administrator may approve, upon recommendation by the Director, Environmental Monitoring and Support Laboratory, Cincinnati, additional alternate test procedures for nationwide use.

TABLE I.—*List of approved test procedures*[1]

Parameter and units	Method	1974 EPA methods	14th ed. standard methods	References (page nos.) Pt. 31 1975 ASTM	References (page nos.) USGS methods[2]	Other approved methods
1. Acidity, as $CaCO_3$[3], milligrams per liter.	Electrometric end point (pH of 8.2) or phenolphthalein end point.	1	275(44)	116	40	[4](607)
2. Alkalinity, as $CaCO_3$[3], milligrams per liter.	Electrometric titration (only to pH 4.5) manual or automated, or equivalent automated methods.	3 5	275	111	41	[4](607)
3. Ammonia (as N), milligrams per liter.	Manual distillation[5] (at pH 9.5) followed by nesslerization, titration, electrode. Automated phenolate.	149 163 165	419 412 418	237	116	[4](614)
BACTERIA						
4. Coliform (fecal)[6], number per 100 ml.	MPN;[7] membrane filter.		902 907		[8](13)	
5. Coliform (fecal)[9] in presence of colonies, number per 100 ml.	do.[10]		902 923, 927			
6. Coliform (total),[9] number per 100 ml.	do.[10]		916 923		[8](13)	

See footnotes at end of table.

TABLE I.—*List of approved test procedures* [1]—Continued

Parameter and units	Method	1974 EPA methods	14th ed. standard methods	References (page nos.) Pt. 31 1973 ASTM	References (page nos.) USGS methods	Other approved methods
BACTERIA—Continued						
7. Coliform (total) [4] in presence of chlorine, number per 100 ml.	MPN;[5] membrane filter with enrichment.	.....	916 933	.....	.....	.....
8. Fecal streptococci,[4] number per 100 ml.	MPN;[5] membrane filter; plate count.	....	943 944 947	....	[7] (30)	.....
9. Benzidine, milligrams per liter.	Oxidation—colorimetric.[6]	.....	.....	.....	.....	.....
10. Biochemical oxygen demand, 5-d (BOD$_5$), milligrams per liter.	Winkler (Azide modification) or electrode method.	.....	543	.....	[7] (30)	[8] (17)
11. Bromide, milligrams per liter.	Titrimetric, iodine-iodate.	14	.....	322	38	.....
12. Chemical oxygen demand (COD), milligrams per liter.	Dichromate reflux.	20	550	472	124	[9] (610) [8] (17)
13. Chloride, milligrams per liter.	Silver nitrate; mercuric nitrate; or automated colorimetric-ferricyanide.	..... 29 31	303 304 613	297 345	.... [8] (16)	[9] (615)
14. Chlorinated organic compounds (except pesticides), milligrams per liter.	Gas chromatography [10]	.....	.....	.....	.....	.....
15. Chlorine—total residual, milligrams per liter.	Iodometric titration, amperometric or starch-iodine end-point; DPD colorimetric or Titrimetric methods (these last 2 are interim methods pending laboratory testing).	..... 35	315 322 332 329	..... 278	....	....
16. Color, platinum cobalt units or dominant wave length, hue, luminance, purity.	Colorimetric; spectrophotometric; or ADMI procedure.[11]	38 39	64 66	....	57	....
17. Cyanide, total,[12] milligrams per liter.	Distillation followed by silver nitrate titration or pyridine pyrazolone (or barbituric acid) colorimetric.	40	361	503	85	[9] (225)
18. Cyanide amenable to chlorination, milligrams per liter.	....do.....	49	376	505	.....	.....
19. Dissolved oxygen, milligrams per liter.	Winkler (Azide modification) or electrode method.	51 56	443 450	368	126	[9] (609) .....
20. Fluoride, milligrams per liter.	Distillation [6] followed by ion electrode; SPADNS; or automated complexone.	..... 63 59 61	299 304 303 314	..... 307 305	..... 93	....
21. Hardness—Total, as $CaCO_3$, milligrams per liter.	EDTA titration; automated colorimetric; or atomic absorption (sum of Ca and Mg as their respective carbonates).	68 70	202	181	94	[9] (617) .....
22. Hydrogen ion (pH), pH units.	Electrometric measurement.	229	460	178	129	[9] (609)
23. Kjeldahl nitrogen (as N), milligrams per liter.	Digestion and distillation followed by nesslerization, titration, or electrode; automated digestion automated phenolate.	178 165 152	437	....	122	[9] (612) .....
METALS						
24. Aluminum—Total, milligrams per liter.	Digestion [13] followed by atomic absorption [14] or by colorimetric (Eriochrome Cyanine R).	92	152 171	....	[8] (10)	....
25. Aluminum—Dissolved, milligrams per liter.	0.45 micron filtration [15] followed by referenced methods for total aluminum.	.....	.....	.....	.....	.....
26. Antimony—Total, milligrams per liter.	Digestion [13] followed by atomic absorption.[16]	94	.....	.....	.....	.....
27. Antimony—Dissolved, milligrams per liter.	0.45 micron filtration [15] followed by referenced method for total antimony.	.....	.....	.....	.....	.....
28. Arsenic—Total, milligrams per liter.	Digestion followed by silver diethyldithiocarbamate; or atomic absorption.[14] [16]	..... 9 12	253 253 153	....	[8] (31) [8] (37)	.....

See footnotes at end of table.

TABLE I.—*List of approved test procedures*[1]—Continued

Parameter and units	Method	1974 EPA methods	14th ed. standard methods	References (page nos.) Pt. 31 1973 ASTM	References (page nos.) USGS methods[2]	Other approved methods[3]
RESIDUE						
101. Total, milligrams per liter	Gravimetric, 103 to 105° C.	270	91			
103. Total dissolved (filterable), milligrams per liter.	Glass fiber filtration, 180° C.	265	92			
106. Total suspended (nonfilterable), milligrams per liter.	Glass fiber filtration, 103 to 105° C.	268	94			
107. Settleable, milliliters per liter or milligrams per liter.	Volumetric or gravimetric		95			
108. Total volatile, milligrams per liter.	Gravimetric, 550° C.	272	95			
109. Specific conductance, micromhos per centimeter at 25° C.	Wheatstone bridge conductimetry.	275	71	129	143	[4] (608)
110. Sulfate (as SO_4), milligrams per liter.	Gravimetric; turbidimetric or automated colorimetric (barium chloranilate).	277 279	433 436	421 423		[4] (621) [4] (622)
111. Sulfide (as S), milligrams per liter.	Titrimetric—Iodine for levels greater than 1 mg per liter; Methylene blue photometric.	284	503 503		154	
112. Sulfite (as SO_3), milligrams per liter.	Titrimetric, iodine-iodate	285	505	435		
113. Surfactants, milligrams per liter.	Colorimetric (Methylene blue).	287	600	451	[5] (12)	
114. Temperature, degrees C.	Calibrated glass or electrometric thermometer.	290	125		[5] (31)	
115. Turbidity, NTU	Nephelometric	295	132	223	158	

[1] Recommendations for sampling and preservation of samples according to parameter measured may be found in "Methods for Chemical Analysis of Water and Wastes, 1974" U.S. Environmental Protection Agency, Table 2, pp. viii-xiii.

[2] All page references for USGS methods, unless otherwise noted, are to Brown, E., Skougstad, M. W., and Fishman, M. J., "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," U.S. Geological Survey Techniques of Water-Resources Inv., book 5, ch. A1, (1970).

[3] EPA comparable method may be found on indicated page of "Official Methods of Analysis of the Association of Official Analytical Chemists" methods manual, 12th ed. (1975).

[4] Manual distillation is not required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary; however, manual distillation will be required to resolve any controversies.

[5] The method used must be specified.

[6] The 5 tube MPN is used.

[7] Sieyk, K. V. and others, "Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples: U.S. Geological Survey Techniques of Water-Resources Inv. book 5, ch. A4 (1973)."

[8] Since the membrane filter technique usually yields low and variable recovery from chlorinated wastewaters, the MPN method will be required to resolve any controversies.

[9] Adequately tested methods for benzidine are not available. Until approved methods are available, the following interim method can be used for the estimation of benzidine: (1) "Method for Benzidine and Its Salts in Wastewaters," available from Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[10] American National Standard on Photographic Processing Effluents, Apr. 2, 1975. Available from ANSI, 1430 Broadway, New York, N.Y. 10018.

[11] Fishman, M. J. and Brown, Eugene, "Selected Methods of the U.S. Geological Survey for Analysis of Wastewaters," (1975) open-file report 76-177.

[12] Procedures for pentachlorophenol, chlorinated organic compounds, and pesticides can be obtained from the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[13] Color method (ADMI procedure) available from Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[14] For samples suspected of having thiocyanate interference, magnesium chloride is used as the digestion catalyst. In the approved test procedure for cyanides, the recommended catalysts are replaced with 20 ml of a solution of 340 g/l magnesium chloride ($MgCl_2 \cdot 6H_2O$). This substitution will eliminate thiocyanate interference for both total cyanide and cyanide amenable to chlorination measurements.

[15] For the determination of total metals the sample is not filtered before processing. Because vigorous digestion procedures may result in a loss of certain metals through precipitation, a less vigorous treatment is recommended as given on p. 53 (4.1.4) of "Methods for Chemical Analysis of Water and Wastes" (1974). In those instances where a more vigorous digestion is desired the procedure on p. 52 (4.1.3) should be followed. For the measurement of the noble metal series (gold, iridium, osmium, palladium, platinum, rhodium and ruthenium), an aqua regia digestion is to be substituted as follows: Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of concentrated redistilled HNO_3. Place the beaker on a steam bath and evaporate to dryness. Cool the beaker and cautiously add a 5 ml portion of aqua regia. (Aqua regia is prepared immediately before use by carefully adding 3 volumes of concentrated HCl to one volume of concentrated HNO_3.) Cover the beaker with a watch glass and return to the steam bath. Continue heating the covered beaker for 30 min. Remove cover and evaporate to dryness. Cool and take up the residue in a small quantity of 1:1 HCl. Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentration. The sample is now ready for analysis.

HANDOUT 3
(Continued)

TABLE I.—*List of approved test procedures*[1]—Continued

Parameter and units	Method	1974 EPA methods	14th ed. standard methods	References (page nos.) Pt. 21 1973 ASTM	References (page nos.) USGS methods [2]	Other approved methods
METALS—Continued						
78. Thallium—Total, milligrams per liter.	Digestion [10] followed by atomic absorption.[14]	149				
79. Thallium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total thallium.					
80. Tin—Total, milligrams per liter.	Digestion [10] followed by atomic absorption.[14]	150			[11] (63)	
81. Tin—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total tin.					
82. Titanium—Total, milligrams per liter.	Digestion [10] followed by atomic absorption.[14]	151				
83. Titanium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total titanium.					
84. Vanadium—Total, milligrams per liter.	Digestion [10] followed by atomic absorption [14] or by colorimetric (Gallic acid).	153	182 220	441	[11] (67)	
85. Vanadium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total vanadium.					
86. Zinc—Total, milligrams per liter.	Digestion [10] followed by atomic absorption [14] or by colorimetric (Dithizone).	156	189 203	345	153	[3](619) [11](37)
87. Zinc—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total zinc.					
88. Nitrate (as N), milligrams per liter.	Cadmium reduction; brucine sulfate; automated cadmium or hydrazine reduction.[18]	201 197 207	423 427 430	338	119	[3](624) [11](25)
89. Nitrite (as N), milligrams per liter.	Manual or automated colorimetric (Diazotization).	213	434		121	
90. Oil and grease, milligrams per liter.	Liquid-liquid extraction with trichloro-trifluoroethane-gravimetric.	229	515			
91. Organic carbon; total (TOC), milligrams per liter.	Combustion—infrared method.[19]	236	532	467	[11] (4)	
92. Organic nitrogen (as N), milligrams per liter.	Kjeldahl nitrogen minus ammonia nitrogen.	175, 199	437		122	[3] (612, 614)
93. Orthophosphate (as P), milligrams per liter.	Manual or automated ascorbic acid reduction.	249 236	451 624	354	121	[3] (621)
94. Pentachlorophenol, milligrams per liter.	Gas chromatography [13]					
95. Pesticides, milligrams per liter.	....do.[13]		535	529	[11] (21)	
96. Phenols, milligrams per liter	Distillation followed by Colorimetric. (4AAP)	241	574	545		
97. Phosphorus (elemental), milligrams per liter.	Gas chromatography [20]					
98. Phosphorus; total (as P), milligrams per liter.	Persulfate digestion followed by manual or automated ascorbic acid reduction.	249 236	478, 451 624	354	123	[3] (621)
RADIOLOGICAL						
99. Alpha—Total, pCi per liter....	Proportional or scintillation counter.		648	551 [11] [3](73+75)		
100. Alpha—Counting error, pCi per liter.	....do		648	551	[11] (79)	
101. Beta—Total, pCi per liter.....	Proportional counter		648	601 [11] [3](73+75)		
102. Beta—Counting error, pCi per liter.	....do		648	606	[11] (79)	
103. (a) Radium—Total, pCi per liter.	....do		661	661		
(b) [226]Ra, pCi per liter.....	Scintillation counter		667		[11] (51)	

See footnotes at end of table.

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[11] As the various furnace devices (flameless AA) are essentially atomic absorption techniques, they are considered to be approved test methods. Methods of standard addition are to be followed as noted in p. 78 of "Methods for Chemical Analysis of Water and Wastes," 1974.

[12] Dissolved metals are defined as those constituents which will pass through a 0.45 μm membrane filter. A preliminary filtration is permissible to free the sample from larger suspended solids. Filter the sample as soon as practical after collection using the first 50 to 100 ml to rinse the filter flask. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Discard the portion used to rinse the flask and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH of 2. Normally, 3 ml of (1:1) acid per liter should be sufficient to preserve the samples.

[13] See "Atomic Absorption Newsletter," vol. 13, 75 (1974). Available from Perkin-Elmer Corp., Main Ave., Norwalk, Conn. 06852.

[14] Method available from Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[15] Recommended methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/l and above are inadequate where silver exists as an inorganic halide. Silver halides such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to a pH of 12. Therefore, for levels of silver above 1 mg/l 20 ml of sample should be diluted to 100 ml by adding 40 ml each of 2M $Na_2S_2O_3$ and 2M NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/l the recommended method is satisfactory.

[16] An automated hydrazine reduction method is available from the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[17] A number of such systems manufactured by various companies are considered to be comparable in their performance. In addition, another technique, based on combustion-coulometric detection is also acceptable.

[18] Goerlitz, D., Brown, E., "Methods for Analysis of Organic Substances in Water": U.S. Geological Survey Techniques of Water-Resources Inv., book 5, ch. A3 (1972).

[19] E. F. Adelson and R. G. Arkman, "Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography," "Journal of Chromatography," vol. 47, No. 3, pp. 421–426, 1970.

[20] The method found on p. 75 measures only the dissolved portion while the method on p. 78 measures only suspended. Therefore, the 2 results must be added together to obtain "total."

[21] Stevens, H. H., Ficke, J. F., and Smoot, G. F., "Water Temperature—Influential Factors, Field Measurement and Data Presentation: U.S. Geological Survey Techniques of Water Resources Inv., book 1 (1975)."

[38 FR 28758, Oct. 16, 1973, as amended at 41 FR 52781, Dec. 1, 1976; 42 FR 3306, Jan. 18, 1977]

§ 136.4 Application for alternate test procedures.

(a) Any person may apply to the Regional Administrator in the Region where the discharge occurs for approval of an alternative test procedure.

(b) When the discharge for which an alternative test procedure is proposed occurs within a State having a permit program approved pursuant to section 402 of the Act, the applicant shall submit his application to the Regional Administrator through the Director of the State agency having responsibility for issuance of NPDES permits within such State.

(c) Unless and until printed application forms are made available, an application for an alternate test procedure may be made by letter in triplicate. Any application for an alternate test procedure under this paragraph (c) shall:

(1) Provide the name and address of the responsible person or firm making the discharge (if not the applicant) and the applicable ID number of the existing or pending permit, issuing agency, and type of permit for which the alternate test procedure is requested, and the discharge serial number.

(2) Identify the pollutant or parameter for which approval of an alternate testing procedure is being requested.

(3) Provide justification for using testing procedures other than those specified in Table I.

(4) Provide a detailed description of the proposed alternate test procedure, together with references to published studies of the applicability of the alternate test procedure to the effluents in question.

(d) An application for approval of an alternate test procedure for nationwide use may be made by letter in triplicate to the Director, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268. Any application for an alternate test procedure under this paragraph (d) shall:

(1) Provide the name and address of the responsible person or firm making the application.

(2) Identify the pollutant(s) or parameter(s) for which nationwide approval of an alternate testing procedure is being requested.

(3) Provide a detailed description of the proposed alternate procedure, together with references to published or other studies confirming the general applicability of the alternate test procedure to the pollutant(s) or parameter(s) in waste water discharges from representative and specified industrial or other categories.

(4) Provide comparability data for the performance of the proposed alternate test procedure compared to the performance of the approved test procedures.

[38 FR 28760, Oct. 16, 1973, as amended at 41 FR 52785, Dec. 1, 1976]

§ 136.5 Approval of alternate test procedures.

(a) The Regional Administrator of the region in which the discharge will occur has final responsibility for approval of any alternate test procedure proposed by the responsible person or firm making the discharge.

(b) Within thirty days of receipt of an application, the Director will forward such application proposed by the responsible person or firm making the discharge, together with his recommendations, to the Regional Administrator. Where the Director recommends rejection of the application for scientific and technical reasons which he provides, the Regional Administrator shall deny the application, and shall forward a copy of the rejected application and his decision to the Director of the State Permit Program and to the Director of the Environmental Monitoring and Support Laboratory, Cincinnati.

(c) Before approving any application for an alternate test procedure proposed by the responsible person or firm making the discharge, the Regional Administrator shall forward a copy of the application to the Director of the Environmental Monitoring and Support Laboratory, Cincinnati.

(d) Within ninety days of receipt by the Regional Administrator of an application for an alternate test procedure, proposed by the responsible person or firm making the discharge, the Regional Administrator shall notify the applicant and the appropriate State agency of approval or rejection, or shall specify the additional information which is required to determine whether to approve the proposed test procedure. Prior to the expiration of such ninety day period, a recommendation providing the scientific and other technical basis for acceptance or rejection will be forwarded to the Regional Administrator by the Director of the Environmental Monitoring and Support Laboratory, Cincinnati. A copy of all approval and rejection notifications will be forwarded to the Director, Environmental Monitoring and Support Laboratory, Cincinnati, for the purposes of national coordination.

(e) Within ninety days of the receipt by the Director of the Environmental Monitoring and Support Laboratory, Cincinnati of an application for an alternate test procedure for nationwide use, the Director of the Environmental Monitoring and Support Laboratory, Cincinnati shall notify the applicant of his recommendation to the Administrator to approve or reject the application, or shall specify additional information which is required to determine whether to approve the proposed test procedure. After such notification, an alternate method determined by the Administrator to satisfy the applicable requirements of this part shall be approved for nationwide use to satisfy the requirements of this subchapter; alternate test procedures determined by the Administrator not to meet the applicable requirements of this part shall be rejected. Notice of these determinations shall be submitted for publication in the FEDERAL REGISTER not later than 15 days after such notification and determination is made.

[38 FR 28760, Oct. 16, 1973, as amended at 41 FR 52785, Dec. 1, 1976]

CRITERIA FOR SELECTION OF AUTOMATIC SAMPLING EQUIPMENT

1. Capability for AC/DC operation with adequate dry battery energy storage for 120-hour operation at 1-hour sampling intervals.

2. Suitability for suspension in a standard manhole while accessible for inspection and sample removal.

3. Total weight, including batteries, under 18 kilograms (40 pounds).

4. Sample collection interval adjustable from 10 minutes to 4 hours.

5. Capability for flow-proportional and time-composite samples.

6. Capability for collecting a single 9.5-liter (2.5-gallon) sample and/or collecting 400-milliliter (0.11-gallon) discrete samples in a minimum of 24 containers.

7. Capability for multiplexing repeated aliquots into discrete bottles.

8. One intake hose with a minimum inner diameter of 0.64 centimeters (0.25 inches)..

9. Intake hose liquid velocity adjustable from 0.61 to 3 meters per second (2.0 to 10 feet per second) with dial setting.

10. Minimum lift of 6.1 meters (20 feet).

11. Explosion-proof.

12. Watertight exterior case to protect components in the event of rain or submersion.

13. Exterior case capable of being locked, including lugs for attaching steel cable to prevent tampering and to provide security.

14. No metal parts in contact with waste source or samples.

15. An integral sample container compartment capable of maintaining samples at 4 to 6°C for a period of 24 hours at ambient temperatures ranging from -30 to 50°C.

16. With the exception of the intake hose, capability of operating in a temperature range from -30 to 50°C.

17. Purge cycle before and after each collection interval and sensing mechanism to purge in event of plugging during sample collection and then to collect complete sample.

18. Field repairability.

19. Interchangeability between glass and plastic bottles, particularly in discrete samplers is desirable.

20. Sampler exterior surface painted a light color to reflect sunlight.

QUALITY ASSURANCE PROCEDURES FOR FIELD ANALYSIS AND EQUIPMENT

Parameter	General	Daily	Quarterly
Dissolved Oxygen Membrane Electrode	Enter the make, model, serial, and/or ID number for each meter in a logbook.	Calibrate meter using manufacturer's instructions or Winkler-Azide method.	Check instrument calibration and linearity using a series of at least three dissolved oxygen standards.
	Report data to nearest 0.1 mg/l.	Check membrane for air bubbles and holes. Change membrane and KCl if necessary.	
		Check leads, switch contracts, etc. for corrosion and shorts if meter pointer remains offscale.	
Winkler-Azide Method	Record data to nearest 0.1 mg/l.	Duplicate analysis should be run as a precision check. Duplicate values should agree within ±0.2 mg/l.	
pH - Electrode Method	Enter the make, model, serial, and/or ID number for each meter in a logbook.	Calibrate the system against standard buffer solutions of known pH value, e.g. 4, 7, and 9 at the start of a sampling run.	Take all meters to the laboratory for maintenance, calibration, and quality control checks.

Parameter	General	Daily	Quarterly
pH (Continued)		Periodically check the buffers during the sample run and record the data and in the logbook.	
		Be on the alert for erratic meter response arising from weak batteries, cracked electrodes, fouling, etc.	
		Check response and linearity following highly acidic or alkaline samples. Allow additional time for equilibration.	
		Check against the closest reference solution each time a violation is found.	
		Rinse electrodes thoroughly between samples and after calibration.	
Conductivity	Enter the make, model, serial and/or ID number for each meter in a logbook.	Standardize with KCl standards having similar specific conductance values to those anticipated in the samples. Calculate the cell constant using two different standards.	Take all meters to lab for maintenance, calibration and quality control checks.

Parameter	General	Daily	Quarterly
Conductivity (Continued)		Cell Constant= Standard Value/ Actual Value Specific Conductance= Reading X Cell Constant	Check temperature compensation.
			Check date of last platinizing and replatinize, if necessary.
		Rinse cell after sample to prevent carryover.	Analyze NBS or EPA reference standard and record actual vs. observed readings in the logbook.
Residual Chlorine Amperometric Titration	Enter the make, model, ID, and/or serial number of each titration apparatus in a logbook. Report results to nearest 0.01 mg/l.	Refer to instrument manufacturer's instructions for proper operation and calibration procedures.	Biweekly: Return instrument to lab for maintenance and addition of fresh, standardized reagents.
Temperature Manual	Enter the make, model, serial, and/or ID number and temperature range for each thermometer.	Check for air spaces of bubbles in the column, cracks, etc. Compare with a known source if available.	Biweekly: Check at two temperatures against a NBS or equivalent thermometer. Enter data in logbook.

Parameter	General	Daily	Quarterly
Temperature Manual (Continued)	All standardization shall be against an NBS or NBS calibrated thermometer. Readings shall agree within ±1°C. If enforcement action is anticipated, calibrate the thermometer before and after analysis. All data shall be read to the nearest 1°C. Report data between 10 and 99°C to two significant figures.		Temperature readings shall agree within ±1°C or the thermometer shall be replaced or recalibrated. Initially and Biannually: Accuracy shall be determined throughout the expected working range of 0 to 50°C. A minimum of three temperatures within the range should be used to verify accuracy. Preferable ranges are: 5-10°, 15-25°, 35-45°C.
Thermistors, Thermographs, etc.	Enter the make, model, serial, and/or ID number of the instrument in a logbook. All standardization shall be against a NBS or NBS calibrated thermometer. Reading should agree within ±1°C. If enforcement action is anticipated refer to the procedure listed above.	Check thermistor or sensing device for response and operation according to the manufacturer's instructions. Record actual vs. standard temperature in logbook.	Initially and Biannually: Accuracy shall be determined throughout the expected working range of 0 to 50°C. A minimum of three temperatures within the range should be used to verify accuracy. Preferable ranges are: 5-10°, 15-25°, 35-45°C.
Flow Measurement	Enter the make, model, serial, and/or ID number of each flow measurement instrument in a logbook.	Install the device in accordance with the manufacturer's instructions and with the procedures given in your manual.	Annually: Affix record of calibration NBS, manufacturer, or other to the instrument log.

Parameter	General	Daily	Quarterly
Automatic Samplers	Enter the make, model, serial, and/or ID number of each sampler in a logbook.		Check intake velocity vs. head (minimum of three samples), and clock time setting vs. actual time interval.

CHAIN OF CUSTODY RECORD

SURVEY

SAMPLERS: *(Signature)*

STATION NUMBER	STATION LOCATION	DATE	TIME	SAMPLE TYPE			SEQ. NO.	NO. OF CONTAINERS	ANALYSIS REQUIRED
				Water		Air			
				Comp.	Grab.				

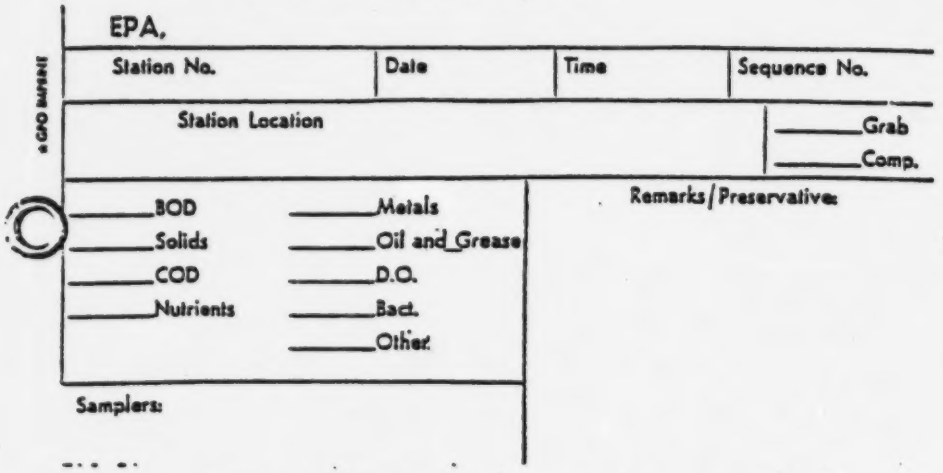
Relinquished by: *(Signature)*	Received by: *(Signature)*	Date/Time
Relinquished by: *(Signature)*	Received by: *(Signature)*	Date/Time
Relinquished by: *(Signature)*	Received by: *(Signature)*	Date/Time
Relinquished by: *(Signature)*	Received by Mobile Laboratory for field analysis: *(Signature)*	Date/Time

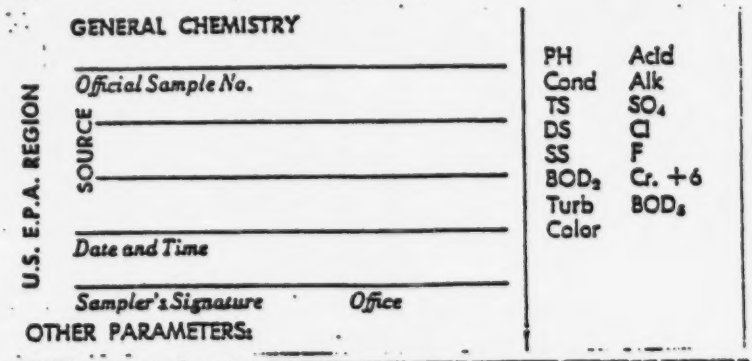
Dispatched by: *(Signature)*	Date/Time	Received for Laboratory by:	Date/Time
Method of Shipment:			

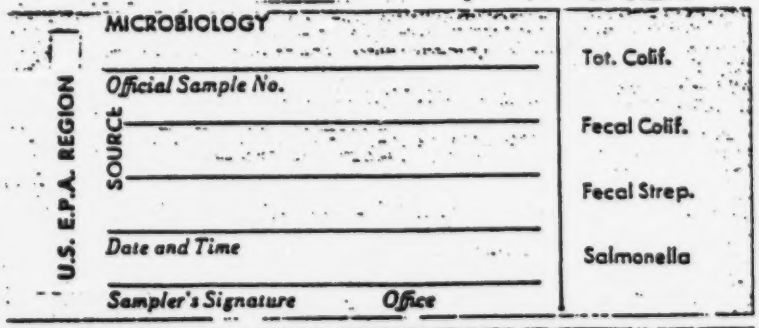
Distribution: Orig. – Accompany Shipment
1 Copy – Survey Coordinator Field Files

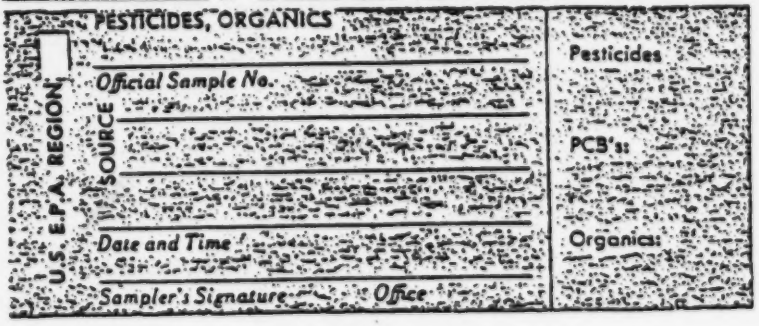
GPO 831-444

SAMPLE IDENTIFICATION LABELS









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